

REFRACTORIES

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APPLICATION OF IR SPECTROSCOPY FOR STUDYING
STRUCTURE FORMATION IN LOW-CEMENT CONCRETESG. S. Rossikhina,¹ N. N. Shcherbakova,² and M. P. Shchedrin³Translated from *Steklo i Keramika*, No. 5, pp. 32 – 34, May, 2009.

Composition optimization and the areas of application of uncalcined refractory concretes dictate the need to study the structure-formation processes occurring in these concretes as temperature increases to the operational level. Methods for using IR spectroscopy to study structure-formation processes in refractory aluminosilicate concretes are examined.

Key words: low-cement refractory concretes, calcium-aluminate cement, structure formation, IR spectroscopy.

The latest trend for lowering the specific usage of refractory materials in furnace lining per unit product is to increase the relative fraction of refractory concrete mixtures and articles made from them [1, 2]. Glass production is no exception. At the present time, low-cement concrete (LCRC) with an aluminosilicate composition with fillers from the chamotte, mullite-alumina, mullite, and mullite-corundum groups are most widely used in glass production lines [3].

Concrete refractory mixes acquire their final properties as the furnace is heated up to working temperature regime, and the heating campaign must correspond to the material used. Pre-formed large-size articles with a complicated configuration and blocks made from the concrete mixes have a special place. The question is whether incorporating the drying and primary low-temperature working of the part into the production process is adequate for the parts to reach their mounting strength and subsequently acquire refractory properties during usage or high-temperature calcination will be required.

The binding systems of LCRC are characterized by a complex composition: high-alumina cement, highly dispersed powder of the refractory component (reactive alumina, spinel, and others), ultrafine microsilica, and diverse complex additives which control the process properties of concrete mixes.

Cements based on calcium aluminates — $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA), $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA_2), $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7) — are used in the materials investigated in the present work — LCRC produced at the Semiluki Refractory Works. The formation of the structure of a binder based on calcium – aluminate cement consists of the following basic stages [1, 4].

Stage	Mineral formation
Setting or hydration at the temperature of the surrounding medium	$\text{Al}(\text{OH})_3$ (gel) $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ (CAH_{10})
Removal of free and surface water at 110°C	$\text{Al}(\text{OH})_3$ (gel) $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$
Removal of water of crystallization at $400 - 600^\circ\text{C}$	$\text{CaO} \cdot \text{Al}_2\text{O}_3$ Al_2O_3 (A)
Sintering at temperatures, $^\circ\text{C}$:	
600 – 1000, 1000 – 1300.	$\text{CaO} \cdot \text{Al}_2\text{O}_3$ $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ Al_2O_3
1400	$\text{CaO} \cdot \text{Al}_2\text{O}_3$ $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (CA_6)

At the initial stages of solidification the binding component of the cement undergoes hydration, as a result of the interaction with water, which results in the formation of a number of hydrate phases. As the crystals of these phases age, a

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framework which gives the concrete its strength at room temperature is formed. The bonding ultimately developed between the cement and filler particles is not present at this stage; as water is removed, some disordering occurs and is compensated at the sintering stage.

Water is present in refractory concretes as free water in large pores, in capillary pores (physically bound water), as well as in the structure of the hydrates — intermediate compounds (chemically bound water). During the drying process the water evaporates and is removed from pores along pore channels. When the temperature rises sharply, the appearance of vapor in the thin capillaries can result in the development of substantial stresses and subsequent formation of cracks — surface cracks and cracks passing through the entire thickness of the material — as well as in the appearance defects, such as swelling of the open surface and stratification of the parts along their thickness dimension.

Concrete parts are heat-treated (up to 380°C) at the manufacturing plant. The physically bound water and most of the chemically bound water are removed during this process. The presence of residues of chemically bound water and the incompleteness of the structure formation process in refractory concrete could have a negative effect on the behavior of concrete as the furnace is maneuvered into the working regime.

At the start of the thermal maneuvering of the refractory lining heat transfer occurs from the outer surfaces toward the center of a part; the temperature – moisture conditions are different at the outer and inner layers, the temperature of the inner layers of the heated part being lower than the temperature of the outer layers. In practice, the temperature of the outer layers is close to that of the surrounding medium, while the temperature of the inner layers reaches the same value only after several hours. Under such conditions it is possible that the presence of the water will affect the state of the concrete lining.

On this basis, to choose the initial thermal maneuvering and operating regimes of refractory concretes it is of interest to investigate the water content of concrete parts heat-treated at the manufacturing plant as well as the processes leading to structure formation in refractory concretes as temperature increases.

The main problems of the investigation of refractory concrete at this stage are to determine the required heat-treatment temperature for the parts before shipment to the customer and to determine the form in which water is present in material treated at different temperatures.

To increase measurement accuracy, samples of concrete as well as specially prepared binder were investigated, since the hydration reaction occurs only in the binder; the chamotte filler is neutral. IR spectroscopy was used to determine OH_n^- groups. This method makes it possible to determine the type and arrangement of water molecules in the silicate structure. A host of information about the arrangement and structure of the binding phases of particular groups can be

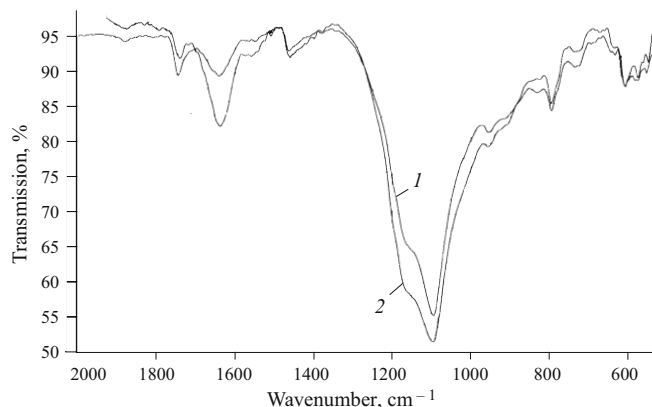


Fig. 1. IR absorption spectra of refractory concrete after heat-treatment: 1) in an electric furnace, first at 380°C and then at 1000°C; 2) in an electric furnace at 380°C followed by soaking in a float bath at 900°C.

obtained by analyzing the IR spectra. Since absorption bands are unique to each compound, the IR spectrum is a fine characteristic of a substance and serves as a criterion for establishing whether or not two compounds are identical [5].

A procedure was developed for preparing the samples. The IR spectra of the raw materials used in the LCRC binders as well as the IR spectra of the calcined chamotte refractories, the binder, and the concrete heat-treated at high temperatures were obtained. An Infracum FT-81 Fourier spectrometer was used to record spectra in pellets with potassium bromide and in Vaseline oil to determine the presence of water.

The fundamental absorption bands in the IR spectra obtained for chamotte, binder, and concrete are identical. This shows that during heat-treatment at 1000°C the finely dispersed components of the refractory concrete matrix interact with one another. The phase composition of the binder is similar to that of the clay binder in classical fired chamotte refractories, and a bond is established in the matrix not only by calcium aluminates, which is determined by petrographic investigations performed in parallel [6].

The IR absorption spectra of concrete heat-treated successively to 380 and 1000°C in an electric furnace and of concrete heat-treated to 380°C and then soaked under the conditions of a commercial float-line at the Saratov Glass Institute at temperature above 900°C are presented in Fig. 1. Comparing the spectra shows that the curves have similar peaks; therefore, processes similar to those occurring during calcination also occur during operation, and uncalcined parts pre-heat-treated at temperature no higher than 400°C can be used.

Figure 2 displays the IR spectra of hardened concrete after soaking at 110°C — the absorption bands of water at 3526 and 3470 cm^{-1} are seen together with bands in the region 3657 – 3607 cm^{-1} , which are characteristic for Al – OH bonds — as well as the spectrum of the binder used in this

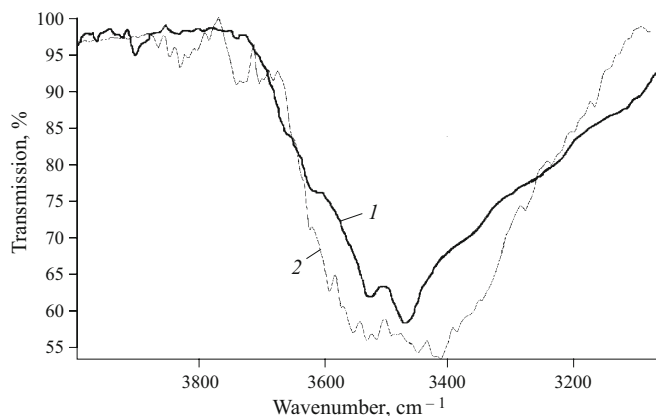


Fig. 2. IR absorption spectra of materials (binder – Vaseline oil) with different heat-treatment temperature in the range 3700 – 3100 cm^{-1} (presence of OH_n^- groups): 1) hardened concrete after soaking at 110°C; 2) binder used in this concrete after heat-treatment at 380°C.

concrete, heat-treated to 380°C, attesting the presence of a water phase.

The IR spectra of the initial materials showed that a water phase is present only in samples of uncalcined clay and cement. In all other samples of the binder and concrete, including samples which were calcined at high temperatures, water is present (in trace quantities, as the very weak absorption bands attest) in the structure as hydroxonium ions H_2O^+ and hydroxyl groups OH^- .

The role of these particles in the transformation of aluminosilicates and how these particles are held in the structure at such high temperatures need to be determined. Probably, this is water bound by donor-acceptor and hydrogen

bonds with other groups in the structure, or it could be water from atmospheric air.

$\text{Ca}-\text{O}$, $\text{K}-\text{O}$, and $\text{Na}-\text{O}$ bonds, i.e., bonds of alkali and alkali-earth metals, are not represented in the IR vibrational spectra. Therefore, no free CaO , which is dangerous because of its reactive power, is found.

In summary, IR absorption spectra can be used to investigate the composition of the structural components of both calcined and uncalcined low-cement concretes.

IR spectroscopic investigations considerably augment the picture obtained for the structure of aluminosilicate refractory concrete composites by x-ray, petrographic, and other methods of studying structure.

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